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(54) **Use of organic phosphonic or phosphinic acids, or of oxides, hydroxides or carboxylic acid salts of metals as thermal stabilizers for polyhydroxyalkanoates**

Verwendung von organischen Phosphon- oder Phosphinsäuren, oder von Metall-oxiden oder -hydroxiden, oder von Carbonsäuresalzen eines Metalls als Hitzestabilisatoren für Polyhydroxyalkanoate

Utilisation des acides phosphoniques ou phosphiniques organiques, ou des oxides, hydroxides ou des sels des acides carboxyliques comme stabilisateurs de chaleur pour des polyhydroxyalkanoates

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(73) Proprietor: **METABOLIX, INC.**
Cambridge, MA 02139 (US)

(72) Inventors:
• **Asrar, Jawed**
Englewood, CO 80111 (US)
• **Pierre, Jean R.**
St.-Denis 5081 (BE)

(74) Representative: **Probert, Gareth David et al**
Potter Clarkson LLP
Park View House
58 The Ropewalk
Nottingham
NG1 5DD (GB)

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EP-A1- 0 400 855 **WO-A1-94/28061**
WO-A1-99/05207 **US-A- 5 646 217**

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Description

[0001] This invention relates generally to the thermal stabilisation of biodegradable polyester compositions and in particular of high molecular weight polyhydroxyalkanoates (PHAs) containing one or more plasticizers. It also relates to the use of such compositions in the production of PHA shaped objects/articles.

BACKGROUND OF THE INVENTION

[0002] There has been considerable interest in recent years in the use of biodegradable polymers to address concerns over plastic waste accumulation. The potential worldwide market for biodegradable polymers is enormous (> 10 B lbs/yr). Some of the markets and applications most amenable to the use of such biopolymers involve those having single, short use applications, including packaging, personal hygiene, garbage bags, and others. These applications, although poorly suited for recycling, are ideally suited for biodegradation through composting.

[0003] PHA biopolymers are polyesters produced by numerous microorganisms in response to nutrient limitation. The commercial potential for PHA spans many industries, and is derived primarily from certain advantageous properties which distinguish PHA polymers from petrochemical-derived polymers and other polymers derived from renewable resources, namely excellent biodegradability and/or natural renewability compared to the petrochemical-derived polymers, and hydrophobicity compared to other polymers derived from renewable resources.

[0004] Widespread use and acceptance of PHA, however, has been somewhat hindered by certain undesirable chemical and physical properties of these polymers. For example, PHA is one of the most thermosensitive of all commercially available polymers. As such, a dramatic rate of polymer degradation is observed at the temperatures typically required for conventional processing of PHA into end-products such as films, coatings, fibers etc. An additional limitation of the potential utility of PHA polymers relates to the observation that certain characteristics such as ductility, flexibility and elongation of the polymer diminish over time. This rapid "aging" of certain PHA-derived products is unacceptable their intended useful life. The success of PHA as a viable alternative to both petrochemical-derived polymers and to non-PHA biodegradable polymers, will depend upon novel approaches to overcome the unique difficulties associated with PHA polymer processing and with products derived therefrom.

[0005] Polymeric films with properties suitable for diverse applications have been difficult to prepare using PHAs due to their frequently unacceptable mechanical characteristics, for example poor melt strength, rapid aging, and brittleness.

[0006] GB 2,243,327 teaches that biodegradable PHA

polymers, such as polyhydroxybutyrate-co-valerate (PHBV) copolymer, cannot be formed into thin films while maintaining the required strength and tear resistance for applications such as a diaper backsheet. This problem was addressed by combining a thin biodegradable thermoplastic polymer film into a sheet laminate with at least one layer of a fiber substrate comprised of biodegradable fibers. However, a cast film of PHBV (6.5% HV) 20 - 24 microns thick when laminated with a rayon nonwoven showed elongation at break of less than 10% in the machine direction which was less than that for the rayon portion alone.

[0007] U.S. Patent No. 4,880,592 discloses a means of achieving a free-standing PHBV film for diaper backsheet applications by coextruding the PHBV between two layers of sacrificial polymer, for example polyolefins, stretching and orienting the multilayer film, and then stripping away the polyolefin layers after the PHBV has had time to crystallize. The PHBV film is then laminated to either water soluble films or water insoluble films such as PVDC or other polyolefins.

[0008] WO 94/00293 discloses multilayer films wherein the PHBV component may be coextruded as an internal layer surrounded by outer layers of films (e.g. biodegradable films) to be used in the application (e.g. diaper films) so that the external layers are not stripped away from the PHBV layer. They remain as an integral part of a biodegradable multilayer film.

[0009] EP 736,563 describes a process for producing cast and blown films from PHBV copolymers that have been compounded with plasticizers, nucleating agents and/or other additives. No specifications of the copolymer were disclosed other than an HV content of 4-16%. The molecular weights of the PHBV powder used in the examples ranged up to 520,000 before compounding and extrusion into pellets. In their disclosed process, films of the compounded PHBV were extruded on a preformed supportive bubble of EVA-resin or LDPE with MFI less than 2.5 g/10min. WO 94/28061 describes granules of PHA plasticized with polyester adipates. US 56 46 217 describes granules of PHA comprising a transesterification catalyst and a plasticizer.

[0010] Thus, attempts to use PHAs in the production of films and other shaped objects have generally resulted in less than desirable properties. It has been difficult, for example, to develop a continuous process for film production which does not depend upon the presence of one or more non-PHA polymer layers in order to improve film processability and/or properties. It is desired, therefore, to develop methods and compositions useful in producing PHA shaped articles having improved overall mechanical characteristics as required for the numerous applications in which resulting plastic articles are typically employed. Furthermore, it is desired that the means to produce improved PHA products be a simple and rapid process that is easily amenable to large scale production, where the PHA articles do not require the presence of non-PHA polymeric materials to achieve acceptable

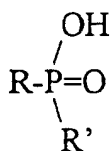
processing performance and/or product properties.

SUMMARY OF THE INVENTION

[0011] The present invention describes the use of certain compounds as thermal stabilizers in pellet compositions comprising PHA, wherein the Mw of the PHA in the pellets is preferably greater than 470,000. The pellets are normally produced by melting PHA powder having a Mw greater than 500,000, extruding a strand of the melted PHA, cooling and crystallizing the extruded strand and cutting the strands into pellets. The pellets so produced are suitable for use in the production of numerous PHA end products by extrusion, molding, coating, spinning and calendaring operations, in particular extrusion blow molded and stretch blow molded containers and bottles, calendered and thermoformed sheets and general extruded parts. The pellet compositions are particularly useful in the production of blown and cast free-standing films as described herein.

[0012] The PHA pellet compositions include one or more polyester plasticizers in accordance with claim 1.

[0013] The thermal stabilizers comprise compounds having the following general structure:



where R' is R or OH, and R is a branched or unbranched saturated C₁-C₃₀ group, a branched or unbranched unsaturated C₂-C₃₀ group, a C₆-C₃₀ aromatic group, or a saturated or unsaturated C₆-C₃₀ cycloaliphatic group. The compounds may contain one or more O, N or S atoms in the alkyl chains and may optionally be substituted with one or more groups selected from hydroxyl, halo, carboxylic acid or ester, cyano, aryl, amino, hydroxylamino, mono-, di-, or trialkyl amino or phosphonic acid.

[0014] Examples of suitable thermal stabilizers of this class of phosphorous-containing compounds include cyclohexylphosphonic acid, 1-cyclohexenylphosphonic acid, 1-hydroxycyclohexenylphosphonic acid, 1-hexanephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, dicyclohexylphosphonic acid and 2,4,4-(trimethylpentyl)cyclohexylphosphonic acid.

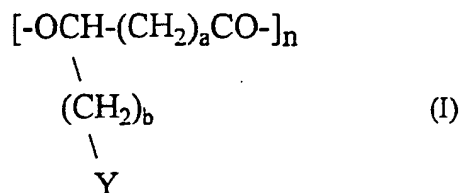
[0015] The thermal stabilizer can also comprise oxides, hydroxides, and saturated or unsaturated carboxylic acid salts of a metals from Groups I to V of the Periodic Table. For example, calcium stearate, barium stearate, magnesium stearate, zinc stearate, and zinc oxide are particularly suitable for use as PHA thermal stabilizers according to the present invention. The thermal stabilizer may comprise one of the disclosed compounds or may comprise a mixture thereof.

[0016] When thermal stabilizers of the present invention are used, less PHA Mw loss is observed when compounding PHA powder into PHA pellets, and when processing PHA pellets into PHA films. As such, pellet compositions suitable for producing PHA films can have a PHA Mw as low as about 435,000, while still maintaining the ability to produce film having the desired Mw of greater than 420,000. Similarly, if a thermal stabilizer is present when producing the 435,000 Mw PHA pellets from PHA powder, the Mw of the PHA powder can be as low as about 480,000.

[0017] The thermally stabilized PHA compositions are useful for the production of polymeric objects for numerous applications. The objects can be produced, for example, by extrusion, molding, coating, spinning and calendaring operations, in particular extrusion blow molded and stretch blow molded containers and bottles, cast and extruded films, calendered and thermoformed sheets, general extruded parts, solution and melt spun fibers, and foamed materials and products.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0018] PHAs are biodegradable polymers or copolymers having the following general structure for one or more of the repeating units:



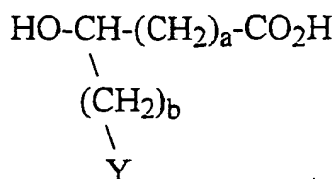
where a is 0 to 6, b is 0 to 15, Y is H, F, Cl, Br, CN, OH, CO₂H, CO₂R (where R is alkyl, benzyl etc.), methyl, cyclohexyl, phenyl, p-nitrophenoxy, p-cyanophenoxy, phenoxyl, acetoxy, vinyl, 2-propyl, 2-butyl, 2-pentyl, 2-hexyl, etc., and n is an integer typically between 10 and 25,000. The pendant groups of the repeating units may contain additional functionalization such as double bonds, epoxidized double bonds, hydroxyl groups, alkyl groups, alkenyl groups etc. or combinations thereof. The polymer main chain can contain up to 8 carbons in the repeating units and there may be additional functionalization in or on the main chain such as double bonds, alkyl groups, alkenyl groups, hydroxyl groups etc. or combinations thereof.

[0019] The PHA is preferably one capable of being biologically produced, for example in a plant or microbial organism. Most typically, it is a fermentation product, particularly of a microbiological process, whereby a microorganism lays down polyhydroxyalkanoate during normal or manipulated growth. Manipulation may be achieved by removing or failing to produce one or more nutrients necessary for cell multiplication. Numerous

microbiological species are known in the art to be suitable for the production of polyhydroxyalkanoate polymers (see for example, Anderson and Dawe Micro. Rev. 54 (4): 450-472, 1990). The microorganisms may be wild type or mutated or may have the necessary genetic material introduced into it, for example by any of the methods or recombinant DNA technology. It is to be emphasized that it is not necessary for the PHA-producing organism to be a microorganism, but at present such organisms are preferred.

[0020] The PHAs preferably have as constituents hydroxyalkanoates (HA) monomers which are substrates for PHA synthase enzymes. Biologically-produced PHA polymers are the product of PHA synthase microbial enzymes, and are produced in either a bacterial cell which naturally contains a PHA synthase, or in a bacterial or other cell type, for example a plant cell, which has been genetically engineered to express such an enzyme. The microbial PHA synthase enzymes have broad substrate ranges and are capable of incorporating a large number of HA monomers as constituents of biosynthetic PHA depending upon growth conditions, precursor substrate availability, and the source of the PHA synthase enzyme. The diversity in composition of biosynthetic PHA polymers is underscored by the fact that at least 91 HA monomers have been identified as substrates for PHA synthases (Steinbüchel, A. and Valentin, H. FEMS Micro. Letters 128 (1995) 219-228).

[0021] Suitable HA monomers can include those having the following formula:



where a is 0 to 6, b is 0 to 15 and Y is H, F, Cl, Br, CN, OH, CO₂H, CO₂R (where R is alkyl, benzyl etc.), methyl, cyclohexyl, phenyl, p-nitrophenoxy, p-cyanophenoxy, phenoxy, acetoxy, vinyl, 2-propyl, 2-butyl, 2-pentyl, 2-hexyl, etc. As in the above description, there may be additional functionalization in or on the pendant and/or main chains. The monomers can be homopolymerized or copolymerized either biochemically or synthetically to produce the polymer.

[0022] Preferred HA monomers include those where a=1-4, b=0-15, and Y is H. More preferably, the monomers are those where a=1-2 and b=0-3, and Y is H.

[0023] In a most preferred polymer, the PHA is of formula (I) where a is 1, b is 1 or 2 and Y is H and especially where there are units with b = 1 and b = 2 copolymerized together. Suitable polyesters contain a preponderance of b = 1, especially with at least 70 mol % of such units, the balance being units in which b = 2. Polymer containing

a = 1, b = 1, Y = H as the only units is polyhydroxybutyrate (PHB) polyester while that containing additionally b = 2 is polyhydroxybutyrate-co-valerate (PHBV).

[0024] The polymer can also be a blend of two or more PHAs differing in the value of m. A particular example contains:

- a) polymer consisting essentially of Formula I units in which 2-5 mol % of units have a = 1, b = 2 and Y = H, the rest a = 1, b = 1, and Y = H, and
- b) polymer consisting essentially of Formula I units in which 5-30 mol % of units have a = 1, b = 2 and Y = H, the rest a = 1, b = 1, and Y = H.

[0025] The proportions of the polymer in such a blend is preferably such as to give an average a = 1, b = 2 and Y = H content in the range 2 to 28 mol % and typically 4 to 18 mol %. Thus, in a most preferred form the polymer is a poly (hydroxybutyrate/valerate) copolymer or blend of copolymers.

[0026] The compositions of the invention may contain a blend of biodegradable polyesters. Blends of particular interest are blends of PHA with polycaprolactone, polylactic acid, and cellulose esters and up to 50 % w/w of the blend preferably comprises one or more polymers selected from polycaprolactone, polylactic acid, and cellulose esters.

[0027] As used herein, the term "molecular weight", unless otherwise specified, refers to the weight average molecular weight (M_w) as opposed to the number average molecular weight (M_n). Most synthetic polymers have a broad distribution of molecular weights, and the molecular weights reported for such polymers represent averages, most frequently defined by M_w or M_n according to the following formulas:

$$M_w = \sum_i n_i M_i^2 / \sum_i n_i M_i$$

$$M_n = \sum_i n_i M_i / \sum_i n_i$$

where n_i = the number of molecules of molecular weight M_i. The most commonly used technique for determining M_w and M_n is by gel permeation chromatography (GPC). This method is capable of determining the entire molecular weight distribution of a polymer sample from which molecular weight averages can be determined. Other methods known in the art for determining M_w and M_n include osmometry, scattering and sedimentation (See for example, W. R. Sorensen & T. W. Campbell: Preparative Methods of Polymer Chemistry, Interscience Publishers, NY, 1961).

PHA PELLETS

[0028] For most processes that produce thermoplastic polymer products such as films and molded articles, it is desirable to have a polymer, polymer blend or polymer formulation supplied to the processor in the form of pellets. This allows the polymeric material to be provided to the processor preformulated for a particular application. In addition, the use of pellets are advantageous in that they avoid problems with dust typically encountered when handling powders. Generally, such pellets are prepared by melt extruding continuous strands of a polymer, polymer blend or the polymer formulation and then cutting the strands into pellets of a desired length.

[0029] It has been found that pellets containing PHA of molecular weights greater than 470,000 are extremely useful in the production of PHA films having desirable characteristics not previously observed. For example, due to the low melt strength of PHA, blown PHA films have not been successfully produced without employing the use of a supporting film. The pellet compositions stabilized according to this invention allow for the production of blown and cast free-standing PHA films having excellent properties while not requiring use of a supporting film. The PHA pellet compositions have a desirably low melt flow index (MFI) less than 20, preferably less than 14, and more preferably less than 8 g/ 10min (170° C/5 kg load).

[0030] In addition to their utility in producing PHA films as further described herein, such pellets are also useful in the production of other PHA end products by extrusion, molding, coating, spinning and calendaring operations, in particular extrusion blow molded and stretch blow molded containers and bottles, calendered and thermoformed sheets, general extruded parts, solution and melt spun fibers and foamed materials and products.

[0031] PHA pellets having high molecular weights have been difficult to produce due to the thermosensitivity of PHA at the processing conditions typically used in the art for pellet production. It is well known in the art that high temperatures produce very rapid PHA degradation. (See for example, Grassie, N., Murray, E. J. and Holmes, P.A.-Polym. Degrad. Stab. 6, pp. 47,95,127 (1984)). The processing conditions disclosed herein serve to minimize the thermal degradation of PHA during processing into pellets. Factors which can effect such degradation include the temperature at which extrusion is performed, the time of exposure to such temperatures, screw speed, shear heating, and screw and die design.

[0032] The pellets are generally produced by extrusion of PHA powder under conditions of low shear and temperature control, either in a single or twin screw extruder. For example, the pellets can be produced using a single screw extruder with a short barrel length (L/D=20) and a low to medium screw speed while maintaining the melt temperature below about 170°C, cooling and crystallizing an extruded strand into a long water bath maintained at 55 to 60° C, and cutting the strand into pellets. The

present method allows for the production of high molecular weight PHA pellets without excessively compromising the stability of the polymer in response to the conditions required for their production.

[0033] It was unexpected that only when PHA in the pellets was of a Mw greater than 470,000 would the pellets be processible into self-supporting blown films. The molecular weight of the PHA in the pellet compositions is determined in part by the molecular weight of the PHA powder used as the starting material to make the pellets. Thus, when making the pellets, it is necessary to choose a suitable molecular weight of the PHA powder and to utilize appropriate processing conditions in order to arrive at pellets having the desired Mw greater than 470,000. Under the processing conditions disclosed above and in the Examples which follow, it is typical to observe about 10 to 30 % reduction in molecular weight of the PHA in the pellets compared to the molecular weight of the PHA in the powder used to produce them. Thus, the PHA in the powder used to produce the PHA-containing pellets typically has a Mw greater than 500,000.

PLASTICIZERS

[0034] The PHA pellets contain one or more plasticizers. Plasticizers for use in the PHA pellet compositions are known to the skilled individual in this art, particularly those described in WO 94/28061. Such plasticizers are well suited for applications where improved impact strength and/or ductility are important.

[0035] The plasticizer is a material capable of plasticizing PHA, i.e. capable of improving the ductility of the polyester and especially a material capable of plasticizing PHB or PHBV. There may be one or more plasticizers present. For the ratio of such plasticizers to PHAs, the range up to 40 phr w/w (particularly 1 to 40 phr w/w) includes most of the likely uses and, for making effectively rigid but not brittle articles, the range 5-25 phr w/w is generally suitable.

[0036] Suitable plasticizers are (in the description, examples and claims herein a * indicates a trade name or registered trademark) adipic esters, such as poly(1,3-butylene glycol-co-1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer*S409A; Mw = 3700, available from Solutia Inc.), poly(neopentyl glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer*S433; Mw = 3500, available from Solutia Inc.), poly(1,3-butylene glycol adipic acid) untermiated (Santicizer*S430; Mw = 2500, available from Solutia Inc.), poly(1,3-butylene glycol adipic acid) untermiated (Santicizer*S421; Mw = 1250, available from Solutia Inc.), poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol (Santicizer*S438; Mw = 1900, available from Solutia Inc.), poly(neopentyl glycol adipic acid) terminated with 2-ethylhexanol (Santicizer*S435; Mw = 2500; available from Solutia Inc.), poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol (Santicizer *431;

Mw = 1200; available from Solutia Inc.), poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2 ethylhexanol (Santicizer *S4212; Mw = 950; available from Solutia Inc.), poly (1,3-butylene glycol adipic acid) terminated with mixed fatty acids (Santicizer *S405; Mw = 2000; available from Solutia Inc.), poly(1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer* S436; Mw = 3500; available from Solutia Inc.), poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol (Santicizer *S449; Mw = 3700; available from Solutia Inc.), poly(1,4-butylene glycol adipic acid), or poly(1,4-butylene glycol-co-ethylene glycol adipic acid).

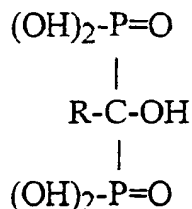
[0037] The composition may contain one or more plasticizers selected from those defined herein and may additionally contain one or more plasticizers previously known to plasticize polyhydroxyalkanoates, for example, citrates containing doubly esterified hydroxycarboxylic acids having at least 3 ester groups in the molecule, glycerol triacetate and glycerol diacetate.

[0038] The compositions can additionally contain the usual polymer processing additives such as fillers, fibers, nucleants, and pigments such as titanium dioxide. It can be in the form of moldings, extrudates, coatings, films or fibers, including multilayer coatings, films or fibers. Because many of the above plasticizers provide improved elongational properties that can be better sustained over time than the properties of non-plasticized materials, intermediate forms of the plasticized compositions, such as sheets and films, are advantageous since they would retain sufficient properties for forming into final products over a period of several months.

NUCLEANTS

[0039] Nucleants are also typically used in producing the PHA pellets. Suitable nucleants can be selected from those known in the art, for example particulate nucleants such as saccharin, talc, boron nitride, ammonium chloride, PHB seed crystals, "polymer soluble" nucleants such as organic phosphonic acids and their combinations with stearic acid salts (see for example WO 91/19759).

[0040] A preferred nucleant is one having the following structure:



where R can be hydroxy, hydrogen, C1-C25 alkyl groups (with or without one or more substituent groups such as -OH, -CO₂H, -Cl, -Br, -NH₂, -N(alkyl)H or N(alkyl)₂),

cycloalkyl groups, aryl or arylalkyl groups (such as phenyl, benzyl, etc. with or without substituents on the aromatic rings). Synthesis of such compounds can be achieved, for example, by reaction of organocarboxylic acids, PC13 in an aqueous medium. The compounds and their syntheses have been described in the prior art for use as water treating chemicals, detergent ingredients, etc. (for example see U.S. 3,855,284, U.S. 3,400,147, U.S. 3,400,150, U.S. 4,254,063, Aus. 599,950, FR 1,521,961 and CA 93:182031). The synthesis can also be applied to dibasic acids such as adipic acid, succinic acid, etc. to give the corresponding tetrakis phosphonic acid (i.e., di-ODPAs) which can also be used as nucleants. For example, with adipic acid, 1,6-dihydroxy-1,6-dihexanediylidene tetraphosphonic acid is obtained (Aus. 599950). Other compounds that can be used as nucleants include methylene diphosphonic acid (PL 131549) and carbonyl diphosphonic acid (CA 93:182031). Such compounds are herein sometimes referred to as organodiphosphonic acids or ODPAs, which is term intended to include both ODPAs and di-ODPAs. The ODPAs or di-ODPA may also be formed in situ, for example by reaction of the corresponding phosphinic acid.

[0041] Preferred ODPAs include 1-hydroxy-lower alkylidene-1,1-diphosphonic acids such as 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), 1-hydroxypropylidene-1,1-diphosphonic acid, 1-hydroxybutylidene-1,1-phosphonic acid, 1-hydroxycyclohexylidene-1,1-diphosphonic acid. In a most preferred nucleant, both acid moieties are phosphonic acid moieties, R1 is a methyl group and R2 is hydroxy group (i.e., HEDP). HEDP is available as a mixture of HEDP in water from Monsanto Company (800 N. Lindbergh, St. Louis, MO 63167) under the tradename DEQUEST 2010. The ODPAs are used in amounts typically in the range of 0.01 - 5.0 phr (parts per hundred resin), more preferably about 0.02 - 1.0 phr, most preferably 0.02 - 0.5 phr.

[0042] The nucleants can further be metallic salts of ODPAs, preferably mono-metallic salts. However, it is generally preferred that not all, e.g., less than 70%, more preferably less than 60% of the phosphonic acid moieties are involved in the salt formation since it has been found that excessive salt formation may adversely influence the effectiveness of certain nucleants.

[0043] Organic metal salts and/or certain inorganic compounds can be used to further improve nucleation activity and/or reduce the extent of discoloration and/or improve the clarity of PHA-derived products when used in combination with the ODPAs of the invention. The organic metal salt is preferably an organic acid salt, more preferably a fatty acid metal salt. The inorganic compound is preferably a metal oxide, a metal hydroxide or a metal carbonate. Suitable metals include those selected from Groups I to V of the periodic table, preferably aluminum, antimony, tin, sodium, calcium, magnesium, barium or zinc. Most preferably the metal is one which has benign environmental and toxicological properties

such as magnesium, calcium and barium. Preferred fatty acids include stearic acid, palmitic acid, acetic acid, propionic acid, caproic acid, oleic acid, behenic acid and montanic acid. Most preferably, the fatty acid metal salt of the invention is calcium stearate or magnesium stearate which have proven highly effective in combination with ODPAs in nucleating thermoplastic polyesters. The organic metal salt or the inorganic metal oxide, metal hydroxide or metal carbonate is used in an amount typically ranging from 0.001 to 5 phr (parts per hundred of resin), preferably about 0.005 to 2 phr, and most preferably about 0.01 to 0.5 phr.

[0044] A nucleant formulation preferably comprises organic metal salt (or inorganic metal oxide, metal hydroxide or metal carbonate) and ODPA in weight ratios of about 0.01:1 to 10:1, preferably about 0.05:1 to 7.5:1, and more preferably about 0.1:1 to 5:1. When calcium stearate is used in a preferred nucleant formulation, a 3:1 ratio has been found to provide a suitable solid support for the ODPA-solvent solution and to produce a PHA nucleant with desirable activity.

[0045] The weak organic base is one which is effective in improving the elongational properties and/or clarity of the polymeric material. The weak organic base should be polymer-miscible or -soluble and melt at a sufficiently high temperature so that, if desired, nucleating agent solvent can be readily removed during preparation. The weak organic base preferably comprises a mono-, bis-, or tri- fatty acid amide, as these generally exhibit good hydrolytic stability in the presence of ODPAs. More preferably, the weak organic base is a stearamide, for example ethylene bistearamide (EBS), available from Lonza or Henkel under the tradename Acrawax C or Loxamid EBS. The weak organic base is typically present in the polymeric compositions in an amount between about 0.01 to 9.0 phr, preferably between about 0.05 to 1.0 phr, most preferably about 0.1 to 0.5 phr.

[0046] One nucleant system that can be used comprises phosphonate/calcium stearate/EBS present in ratios effective for nucleating PHA and producing PHA articles having excellent clarity, color, elongational and tensile properties. This system is soluble in the polymer and also stabilizes PHA against thermal degradation. The phosphonates that can be used include those described as phosphorous-containing compounds under "PHA Thermal Stabilization" below. This nucleant system is especially suitable for nucleating PHBV to obtain a clear composition for use as a film.

[0047] A most preferred nucleant for use in this invention comprises HEDP/calcium stearate/EBS present in ratios effective for nucleating PHA and producing PHA articles having excellent clarity, color, elongational and tensile properties. Most preferably, the constituents of this formulation are present in weight ratios of about 0.8/1.5/1.7 respectively.

[0048] Suitable levels of such a nucleant formulation to be added to the PHA range from about 0.01 to 5.0 parts per hundred of resin (phr). Preferably, the level of

the nucleant formulation is about 0.05 - 1.0 phr, and most preferably it is about 0.1 - 0.6 phr.

[0049] It is advantageous when preparing the nucleant to dissolve/suspend the ODPA, and optionally the organic metal salt, inorganic metal oxide, metal hydroxide or metal carbonate, and/or the weak organic base, in an effective nucleating agent solvent. Preferably, the solvent is then removed, for example by evaporation under vacuum, giving rise to solids which are ground, pulverized, or otherwise treated so as to produce particles with diameters less than about 710 microns, preferably less than about 350 microns. The term "effective nucleating agent solvent" herein means a solvent which dissolves the ODPA and preferably enhances its nucleation activity but which does not intolerably reduce its effectiveness as a nucleant. Thus, the ODPA prepared using an effective nucleating agent solvent as described herein will have at least as effective nucleation activity, preferably greater nucleation activity, compared to the same ODPA that is not dissolved in an effective nucleating agent solvent during its preparation or use.

[0050] Nucleating agent solvents for use in this invention include but are not limited to C1 to C6 aliphatic mono-, di- and tri-ols such as methanol, ethanol, ethylene glycol, 1- or 2-propanol, propylene glycol, glycerol, 2-methyl-2-propanol, 2-butanol and the like, and further including mixtures of such solvents with each other and with water. Preferred nucleating agent solvents include methanol, ethanol or another lower alcohols, or mixtures of such alcohols with water to allow for easy solvent removal. The nucleating agent solvent needs to be appropriately selected since it has been found that some solvents such as acetone and tetrahydrofuran when used with some ODPAs such as HEDP are not effective nucleating agent solvents. However, it is known that mixtures of solvents, e.g. methanol and acetone, can serve as effective nucleating agent solvents as defined herein even though one of the solvents in the mixture is not an effective nucleating agent solvent when used alone. While all of the solvents which will be effective nucleating agent solvents has not yet been elucidated, a person skilled in the art can readily determine whether a proposed solvent for an ODPA is "effective" by routine experimentation following the description herein.

[0051] It would be understood by one skilled in the art that the PHA pellet compositions may include a number of additives or other components which are commonly included in polymeric materials.

[0052] These may include, for example, dyes, fillers, stabilizers, modifiers, anti-blocking additives, antistatic agents etc.

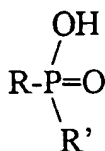
PHA THERMAL STABILIZATION

[0053] It has been found that the presence of certain compounds, hereinafter referred to as thermal stabilizers, can reduce the extent of molecular weight loss due to PHA degradation normally observed during com-

pounding of PHA powder into PHA pellets, and during processing of PHA pellets into end products such as films. Given the extreme thermosensitivity of PHA, the present method is applicable to any situation where it is desirable to minimize PHA degradation during exposure to temperatures or other conditions which would typically cause such degradation.

[0054] Thermal degradation of PHA is generally believed to take place by chain scission involving the formation of a six-membered transition state. Unlike most polymers, where thermal degradation is a free radical process, it has been reported and generally accepted that free radical scavengers and known thermal stabilizers have not been effective in stabilizing PHA against thermal degradation.

[0055] One class of thermal stabilizers of the present invention comprise compounds having the following structural formula:



where R' is R or OH, and R is a branched or unbranched saturated C₁-C₃₀ group, a branched or unbranched unsaturated C₂-C₃₀ group, a C₆-C₃₀ aromatic group, or a saturated or unsaturated C₆-C₃₀ cycloaliphatic group. The compounds may contain one or more O, N or S atoms in the alkyl chains and may optionally be substituted with one or more groups selected from but not limited to hydroxyl, halo, carboxylic acid or ester, cyano, aryl, amino, hydroxylamino, mono-, di-, or trialkyl amino, phosphonic acid, etc.

[0056] Examples of suitable thermal stabilizers of this class of phosphorous-containing compounds include cyclohexylphosphonic acid (DZB), 1-cyclohexenylphosphonic acid, 1-hydroxycyclohexenylphosphonic acid, 1-hexanephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, or dicyclohexylphosphonic acid, 2,4,4-(trimethylpentyl)cyclohexylphosphonic acid. Particularly useful are cyclohexylphosphonic acid and 1-hydroxyethylidene-1,1-diphosphonic acid.

[0057] The present findings suggest that, although random chain scission is likely the main mode of thermally induced PHA degradation, other processes such as thermo-oxidative degradation may also be operative in reducing the Mw of PHA during thermal processing since phosphorous-containing compounds can act as oxygen scavengers.

[0058] Various metal containing compounds can also serve as PHA thermal stabilizers. Metal compounds suitable for use in the present invention include oxides, hydroxides, and saturated or unsaturated carboxylic acid salts of metals from Groups I to V of the Periodic Table.

These can include, for example, compounds of aluminum, antimony, barium, tin, sodium, calcium, magnesium and zinc. The carboxylic acids can include stearates and palmitates. Particularly useful are fatty acid salts such as calcium stearate (CaSt), magnesium stearate (MgSt), zinc stearate (ZnSt), and zinc oxide. While not wishing to be bound by this explanation, it is possible that the ability of such compounds to act as thermal stabilizers may be due to their lubricating effects. This may result in reduced shear heating generated during processing, thereby resulting in less internal polymer heat and therefore less degradation.

[0059] A single thermal stabilizer may be used in an amount sufficient to inhibit PHA degradation. Alternatively, a combination of thermal stabilizers can be used. In one preferred embodiment, both DZB and zinc stearate are dry blended with the PHA powder used to produce PHA pellets. Although a DZB/ZnSt combination has been used as a nucleant system in some settings (see for example WO 91/19759) the ability of such compounds to act as thermal stabilizers for PHA has not been previously recognized. This invention demonstrates that the presence of DZB and ZnSt results in significantly less PHA degradation during the pellet forming process. As a result, PHA pellets extruded with DZB and ZnSt show significantly less molecular weight loss relative to the PHA powder used to produce them than PHA pellets extruded with the commonly used nucleant, boron nitride. Furthermore, when these pellets are melt processed into films, significantly less Mw reduction during film production is observed, as further described below.

SHAPED PHA ARTICLES

[0060] The stabilized pellets are especially useful for making shaped articles such as films, especially for packaging, fibers, non-woven fabrics, extruded nets, personal hygiene products, bottles and drinking vessels, agricultural and horticultural films and vessels, ostomy bags, coated products (such as paper, paperboard, non-woven fabrics), agricultural and horticultural films and vessels, slow-release devices. Alternatively, the polymer composition with suitable additives can be used as an adhesive.

[0061] Extruded PHAs having molecular weights greater than 420,000 provide a desirable combination of melt strength during initial film formation and subsequent drawability sufficient for use in stable blown film and cast film processes.

[0062] The differences in properties for films containing PHA having molecular weights less than 420,000, compared to films containing PHA of higher molecular weights was unexpected. It was further unexpected that even higher molecular weight PHA films (i.e. greater than 420,000) could be produced without encountering processing difficulties due to unacceptably high viscosities. Polymer melt having desired melt and extensional strengths, while maintaining good processibility, were only achieved when the molecular weight of the PHA in

the extruded film was greater than 420,000.

[0063] The PHA films are preferably oriented, either mono- or bi-axially, in order to maximize mechanical properties. Bi-axially oriented means to stretch the film along a direction in which it travels, called the machine direction, and in a direction 90° to the machine direction in the plane of the film, known as the transverse direction, thereby extending length and width of the film to greater than its initial dimensions. Bi-axial orientation may involve simultaneous or sequential stretching. Mono-axial orientation refers to stretching in either the machine direction or the transverse direction, but not both. PHA film compositions of the present invention are formed into films of a uniform thickness ranging from about 75 to 150 microns prior to orientation, and ranging from about 5 to 100 microns after orientation.

[0064] Films typically exhibit elongation to break greater than 65%, preferably greater than 75%, and more preferably greater than 100%. In addition, the tensile strength of the films is typically greater than 50 MPa, preferably greater than 75 MPa, and more preferably greater than 90 MPa.

[0065] The presence of DZB and ZnSt in the pellets used to produce the films resulted in only a 3% PHA Mw loss during film processing compared to 14.1 % when boron nitride was used as a nucleant (see Example 21). Thus, when thermal stabilizers are present in the pelletized PHA, the molecular weight of the PHA in the pellet can be as low as 435,000 while still allowing for the production of blown film containing PHA of the desired molecular weight greater than 420,000.

[0066] It would be understood by one skilled in the art that the PHA film compositions may include a number of additives or other components which are commonly included in polymeric films.

[0067] These may include, for example, dyes, fillers, stabilizers, modifiers, anti-blocking additives, antistatic agents etc.

[0068] The PHA films are useful for numerous applications involving packaging, bags and/or membranes. The films are particularly well suited for production of food and non-food packaging, protecting films, trash bags, blisters, slit film woven bags, composting bags, shopping bags and bubble films.

[0069] In addition to susceptibility of PHAs to thermal degradation, low melt strength and slow crystallization rates further complicate film processing methods. Low polymer melt strength creates a need to operate cast film lines at slow line speeds or to use a supporting film or web onto which the PHBV is cast and later isolated as a free-standing film by peeling away the supporting film. Low melt strength makes it extremely difficult to produce blown film without the use of a supporting blown film. Additionally, when producing blown films, residual tack of the PHA can cause the tubular film to stick to itself after it has been cooled and collapsed for winding.

[0070] Previously, a continuous process for the production of blown and cast free-standing PHA film has

been difficult to develop due in part to poor melt strength of the material. The method involves melt processing PHA, preferably in the form of the PHA pellets of this invention, forming the melt into a film, for example by blowing a bubble through a circular die or by casting on cooling rolls through a T shape flat die, and orienting the film by continuous mono- or bi-axial stretching. The Mw of the PHA in the film is greater than 420,000. The Mw of the PHA in the pellets used to produce the film can be as low as 435,000 while still being suitable for producing film containing PHA of the desired Mw greater than 420,000.

[0071] The films can be formed by a variety of known techniques, such as extrusion processes including calendering, flat die extrusion and film blowing, in addition to casting solutions or suspensions of polymeric compositions followed by solvent recovery.

[0072] This method has been found to be particularly useful in producing blown and cast free-standing films having molecular weights greater than 420,000. Many polymer materials used for industrial and agricultural applications are produced from blown and cast film. However, PHA pellets processible into unsupported film by this approach have been neither described nor characterized as having that capability.

[0073] The molecular weight of the PHA in the pellets is critical in achieving a stable film blowing process in accordance with this method. PHA pellets having molecular weights less than 435,000 are not suitable for the production of blown films due in part to bubble instability caused by low melt strength.

[0074] Film blowing processes are well known in the art (see for example Rosato & Rosato, Plasticizer Processing Data Handbook, Van Nostrand Reinhold (Pub.), NY, 1990). Film blowing typically involves melt extrusion of a tubular preform, cooling the preform, blowing the preform with air such that a stable bubble is formed, collapsing the bubble between nip rolls to produce a film. During blown film processing, the blow up ratio determines the amount of circumferential orientation and the pull rate of the bubble determines longitudinal orientation. With PHA films, mono orientation can be achieved by operating with a puller roll speed to feeder roll speed sufficient to give a draw ratio in the 2-6 range. The cooling rate (air flow), thickness, diameter and height of the bubble are adjusted so that the PHA tubular film is sufficiently crystalline to produce orientation and prevent sticking and blocking, but not too crystalline so as to exhibit undesirable stiffness and brittleness which would prevent the continuous drawing operation.

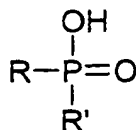
[0075] In orienting film or sheet, a tentering frame may be used which has continuous speed control and diverging tracks with holding clamps. As the clamps move apart at prescribed diverging angles, the hot plastic is stretched in the transverse direction resulting in monodirectional orientation. To obtain bidirectional orientation, an in-line series of heat controlled rolls are located between the extruder and tenter frame. The rotation of each succeed-

ing roller can be increased depending upon the longitudinal stretched properties desired.

Claims

1. Use of a compound selected from:

(a) a compound having the structural formula:



where R' is R or OH, and R is a branched or unbranched saturated C₁-C₃₀ group, a branched or unbranched unsaturated C₂-C₃₀ group, a C₆-C₃₀ aromatic group, or a saturated or unsaturated C₆-C₃₀ cycloaliphatic group; or (b) oxides, hydroxides, and saturated or unsaturated carboxylic acid salts of metals from Groups I to V of the Periodic Table;

as a thermal stabilizer of polyhydroxyalkanoate (PHA) by including the compound in a PHA-containing composition for forming a pellet to inhibit the degradation of PHA during exposure of the composition to temperatures which cause PHA degradation, wherein the PHA-containing composition comprises a plasticizer compound selected from poly(1,3-butylene glycol-co-1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol, poly(neopentyl glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol; poly(1,3-butylene glycol adipic acid) unterminated, poly(1,3-butylene glycol adipic acid) unterminated, poly(1,2-propylene glycol adipic acid-co-phthalic acid) terminated with 2-ethylhexanol, poly(neopentyl glycol adipic acid) terminated with 2-ethylhexanol, poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol, poly(1,3-butylene glycol adipic acid) terminated with mixed fatty acids, poly(1,2-propylene glycol adipic acid) terminated with 2-ethylhexanol, poly(1,2-propylene glycol-co-1,4-butylene glycol adipic acid) terminated with 2-ethylhexanol, poly(1,4-butylene glycol adipic acid) and poly(1,4-butylene glycol-co-ethylene glycol adipic acid).

2. Use according to Claim 1 wherein the compound defined by part (a) of Claim 1 contains one or more O, N or S atoms in the alkyl chain.

3. Use according to Claim 1 or 2 wherein the compound defined by part (a) of Claim 1 is substituted with one

or more groups selected from hydroxyl, halo, carboxylic acid or ester, cyano, aryl, amino, hydroxylamino, mono-, di-, or trialkyl amino or phosphonic acid.

4. Use according to Claim 1 wherein the compound defined by part (a) of Claim 1 is cyclohexylphosphonic acid, 1-cyclohexenylphosphonic acid, 1-hydroxycyclohexenylphosphonic acid, 1-hexanephosphonic acid, 1-hydroxyethylidene 1,1-diphosphonic acid, dicyclohexylphosphonic acid or 2,4,4-(trimethylpentyl)cyclohexylphosphonic acid.

5. Use according to Claim 1 wherein the compound defined by part (b) of Claim 1 is a compound of aluminum, antimony, barium, tin, sodium, calcium, magnesium or zinc.

6. Use according to Claim 1 or 5 wherein the compound as defined by part (b) of Claim 1 is a stearate or palmitate.

7. Use according to Claim 1, 5 or 6 wherein the compound defined by part (b) of Claim 1 is calcium stearate, magnesium stearate, zinc stearate or zinc oxide.

8. Use according to any one of the preceding claims wherein the compound is used as a first thermal stabilizer in combination with a second thermal stabilizer, which second thermal stabilizer is also a compound as defined by Claim 1.

9. Use according to Claim 8 wherein the compound used as a first thermal stabilizer is zinc stearate, and the second stabilizer is cyclohexylphosphonic acid.

10. Use according to any one of the preceding claims wherein the PHA in the polyester pellet composition has a weight average molecular weight of at least 435,000.

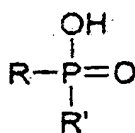
11. Use according to any preceding claim to inhibit the degradation of PHA during the production of a shaped polymeric object comprising melting the composition and producing a shaped object therefrom by extrusion, molding, coating, spinning or calendering operations.

12. Use according to Claim 11 wherein the shaped object is a blown film comprising PHA having a weight average molecular weight of at least 420,000.

Patentansprüche

1. Verwendung einer Verbindung, die ausgewählt ist aus

a) einer Verbindung mit der Strukturformel



wobei R' R oder OH ist und R eine verzweigte oder unverzweigte gesättigte C₁-C₃₀-Gruppe, eine verzweigte oder unverzweigte ungesättigte C₂-C₃₀-Gruppe, eine aromatische C₆-C₃₀-Gruppe oder eine gesättigte oder ungesättigte cycloaliphatische C₆-C₃₀-Gruppe ist, oder b) Oxiden, Hydroxiden und Salzen von Metallen der Gruppen I bis V des Periodensystems gesättigter oder ungesättigter Carbonsäuren

als Wärmestabilisator von Polyhydroxyalkanoat (PHA) durch das Einarbeiten der Verbindung in eine PHA-haltige Zusammensetzung zur Erzeugung eines Pellets für die Hemmung der Zersetzung von PHA während der Exposition der Zusammensetzung gegen Temperaturen, die eine Zersetzung des PHA verursachen, wobei die PHA-haltige Zusammensetzung eine Weichmacherverbindung umfasst, die ausgewählt ist aus Poly(1,3-butylenglycol-co-1,2-propylenglycoladipinsäure) terminiert mit 2-Ethylhexanol, Poly(neopentylglycol-co-1,4-butylenglycoladipinsäure) terminiert mit 2-Ethylhexanol, Poly(1,3-butylenglycoladipinsäure) unterterminiert, Poly(1,3-butylenglycoladipinsäure) unterterminiert, Poly(1,2-propylenglycoladipinsäure-co-phthalsäure) terminiert mit 2-Ethylhexanol, Poly(neopentylglycoladipinsäure) terminiert mit 2-Ethylhexanol, Poly(1,2-propylenglycol-co-1,4-butylenglycoladipinsäure) terminiert mit 2-Ethylhexanol, Poly(1,3-butylenglycoladipinsäure) terminiert mit gemischten Fettsäuren, Poly(1,2-propylenglycoladipinsäure) terminiert mit 2-Ethylhexanol, Poly(1,2-propylenglycol-co-1,4-butylenglycoladipinsäure) terminiert mit 2-Ethylhexanol, Poly(1,4-butylenglycoladipinsäure) und Poly(1,4-butylenglycol-co-ethylenglycoladipinsäure).

2. Verwendung gemäß Anspruch 1, wobei die durch den Teil a) von Anspruch 1 definierte Verbindung ein oder mehrere O-, N- oder S-Atom(e) in der Alkylkette enthält.

3. Verwendung gemäß Anspruch 1 oder 2, wobei die durch den Teil a) von Anspruch 1 definierte Verbindung mit einer oder mehreren Gruppe(n) substituiert ist, die aus Hydroxy, Halogen, Carbonsäure oder Ester, Cyano, Aryl, Amino, Hydroxylamino, Mono-, Di- oder Trialkylamino oder Phosphonsäure ausgewählt ist bzw. sind.

4. Verwendung gemäß Anspruch 1, wobei die durch den Teil a) von Anspruch 1 definierte Verbindung Cyclohexylphosphonsäure, 1-Cyclohexenylphosphonsäure, 1-Hydroxycyclohexenylphosphonsäure, 1-Hexanphosphonsäure, 1-Hydroxyethyliden-1,1-diphosphonsäure, Dicyclohexylphosphonsäure oder 2,4,4-(Trimethylpentyl)cyclohexylphosphonsäure ist.

5. Verwendung gemäß Anspruch 1, wobei die durch den Teil b) von Anspruch 1 definierte Verbindung eine Verbindung von Aluminium, Antimon, Barium, Zinn, Natrium, Calcium, Magnesium oder Zink ist.

6. Verwendung gemäß Anspruch 1 oder 5, wobei die durch den Teil b) von Anspruch 1 definierte Verbindung ein Stearat oder Palmitat ist.

7. Verwendung gemäß Anspruch 1, 5 oder 6, wobei die durch den Teil b) von Anspruch 1 definierte Verbindung Calciumstearat, Magnesiumstearat, Zinkstearat oder Zinkoxid ist.

8. Verwendung gemäß einem beliebigen der vorhergehenden Ansprüche, wobei die Verbindung als ein erster Wärmestabilisator in Kombination mit einem zweiten Wärmestabilisator verwendet wird, wobei dieser zweite Wärmestabilisator ebenfalls eine Verbindung ist, wie sie durch Anspruch 1 definiert ist.

9. Verwendung gemäß Anspruch 8, wobei die als erster Wärmestabilisator verwendete Verbindung Zinkstearat ist und der zweite Stabilisator Cyclohexylphosphonsäure ist.

10. Verwendung gemäß einem beliebigen der vorhergehenden Ansprüche, wobei das PHA in der Polyesterpelletzusammensetzung ein Gewichtsmittel des Molekulargewichts von wenigstens 435 000 hat.

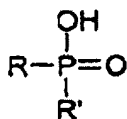
11. Verwendung gemäß einem beliebigen der vorhergehenden Ansprüche zur Hemmung der Zersetzung von PHA während der Erzeugung eines polymeren Formgegenstands, wobei die Verwendung das Schmelzen der Zusammensetzung und das Erzeugen eines Formgegenstands aus ihr durch ein Extrudieren, Formen, Beschichten, Spinnen oder Kalandern umfasst.

12. Verwendung gemäß Anspruch 11, wobei der Formgegenstand eine Blasfolie ist, die PHA mit einem Gewichtsmittel des Molekulargewichts von wenigstens 420 000 umfasst.

Revendications

1. Utilisation d'un composé choisi parmi :

(a) un composé ayant la formule structurale :



dans laquelle R' est R ou OH, et R est un groupe en C₁ à C₃₀ saturé, ramifié ou non ramifié, un groupe en C₂ à C₃₀ insaturé, ramifié ou non ramifié, un groupe aromatique en C₆ à C₃₀ ou un groupe cycloaliphatique en C₆ à C₃₀ saturé ou insaturé ; ou

(b) des oxydes, hydroxydes et sels d'acide carboxylique insaturé de métaux des groupes I à V du tableau périodique ;

en tant que stabilisateur thermique de polyhydroxyalcanoate (PHA) en incluant le composé dans une composition contenant du PHA pour former une pastille afin d'inhiber la dégradation de PHA pendant une exposition de la composition à des températures qui entraînent une dégradation du PHA, dans laquelle la composition comprenant du PHA comprend un composé plastifiant choisi parmi le poly(1,3-butylène glycol-co-1,2-acide 1,2-propylène glycol adipique) terminé par du 2-éthylhexanol ; le poly(néopentyl glycol-co-acide 1,4-butylène glycol adipique) terminé par du 2-éthylhexanol ; le poly(acide 1,3-butylène glycol adipique) non terminé ; le poly(acide 1,3-butylène glycol adipique) non terminé ; le poly(acide 1,2-propylène glycol adipique-co-acide phtalique) terminé par du 2-éthylhexanol ; le poly(acide néopentyl glycol adipique) terminé par du 2-éthylhexanol ; le poly(1,2-propylène glycol-co-acide 1,4-butylène glycol adipique) terminé par du 2-éthylhexanol ; le poly(acide 1,3-butylène glycol adipique) terminé par des acides gras mixtes ; le poly(acide 1,2-propylène glycol adipique) terminé par du 2-éthylhexanol ; le poly(1,2-propylène glycol-co-acide 1,4-butylène glycol adipique) terminé par du 2-éthylhexanol ; le poly(acide 1,4-butylène glycol adipique) et le poly(1,4-butylène glycol-co-acide éthylène glycol adipique).

2. Utilisation selon la revendication 1, dans laquelle le composé défini par la partie (a) de la revendication 1 contient un ou plusieurs atomes O, N ou S dans la chaîne alkyle.

3. Utilisation selon la revendication 1 ou 2, dans laquelle le composé défini par la partie (a) de la revendication 1 est substitué par un ou plusieurs groupes choisis parmi un groupe hydroxyle, halogéno, acide carboxylique ou ester, cyano, aryle, amino, hydroxylamino, mono-, di- ou trialkyl amino ou acide phos-

phonique.

4. Utilisation selon la revendication 1, dans laquelle le composé défini par la partie (a) de la revendication 1 est l'acide cyclohexylphosphonique, l'acide 1-cyclohexénylphosphonique, l'acide 1-hydroxycyclohexénylphosphonique, l'acide 1-hexanephosphonique, l'acide 1-hydroxyéthylidène-1,1-diphosphonique, l'acide dicyclohexylphosphonique ou l'acide 2,4,4-(triméthylpentyl)cyclohexylphosphonique.

5. Utilisation selon la revendication 1, dans laquelle le composé défini par la partie (b) de la revendication 1 est un composé d'aluminium, d'antimoine, de baryum, d'étain, de sodium, de calcium, de magnésium ou de zinc.

6. Utilisation selon la revendication 1 ou 5, dans laquelle le composé tel que défini par la partie (b) de la revendication 1 est un stéarate ou un palmitate.

7. Utilisation selon la revendication 1, 5 ou 6, dans laquelle le composé défini par la partie (b) de la revendication 1 est le stéarate de calcium, le stéarate de magnésium, le stéarate de zinc ou l'oxyde de zinc.

8. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le composé est utilisé comme premier stabilisateur thermique en combinaison avec un second stabilisateur thermique, le second stabilisateur thermique étant également un composé tel que défini par la revendication 1.

9. Utilisation selon la revendication 8, dans laquelle le composé utilisé comme premier stabilisateur thermique est le stéarate de zinc, et le second stabilisateur est l'acide cyclohexylphosphonique.

10. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le PHA dans la composition de pastille de polyester a une masse moléculaire moyenne en masse d'au moins 435 000.

11. Utilisation selon l'une quelconque des revendications précédentes, pour inhiber la dégradation de PHA pendant la production d'un objet polymère façonné comprenant la fusion de la composition et la production d'un objet façonné à partir de celle-ci par des opérations d'extrusion, de moulage, de revêtement, de filage ou de calandrage.

12. Utilisation selon la revendication 11, dans laquelle l'objet façonné est un film soufflé comprenant du PHA ayant une masse moléculaire en masse d'au moins 420 000.

REFERENCES CITED IN THE DESCRIPTION

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